Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

Roughness controlled superhydrophobicity on single nanometer length scale with metal nanoparticles

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A) Methodology

Nanoparticle deposition based on gas phase aggregation is initiated by accelerating an argon plasma onto a copper target. The plasma is made by feeding argon gas in from behind the magnetron head and (ii) applying a potential between the copper disk, which acts as a cathode, and the anode, which sits on top of the disk. The plasma breaks off singular atoms of the copper disk, which form a vapor. This vapor then is transported away from the magnetron head to an aggregation volume, where it is confined and cooled by the local high pressure argon gas. The vapor reaches super-saturation and forms copper clusters, which are deposited onto the sample. Figure A1 shows a schematic of this deposition technique.

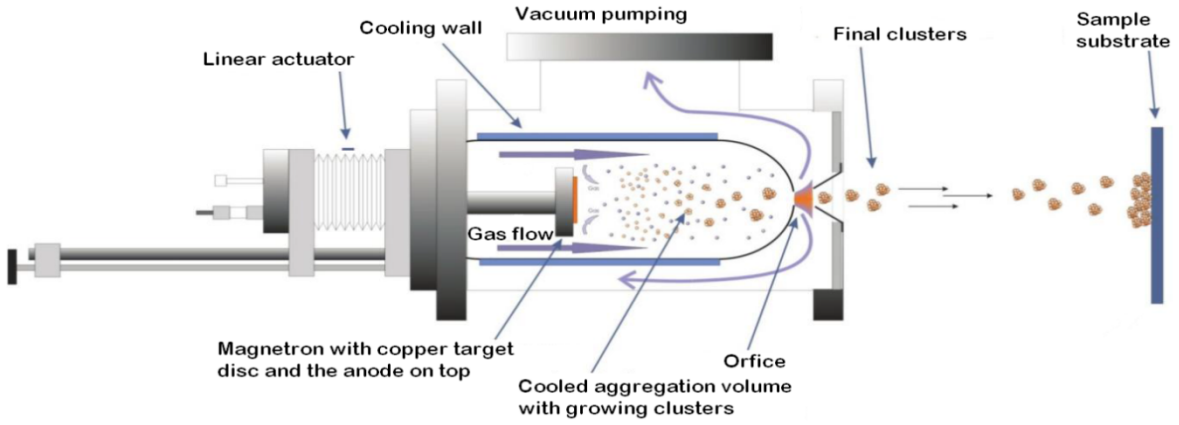

Figure A1: Schematic high pressure NP sputtering unit. Source of image: modified from the Mantis Nanogen 50 Operations Manual.

A 2-inch silicon wafer was prepared for samples by cutting them in square 1 cm^2 pieces. Another 2-inch silicon wafer was coated with a homogeneous 20 nm thick layer of copper as a starting (relatively flat) substrate surface and was also cut in 1 cm^2 pieces. Both these sample surface types were coated with copper NPs with various NP sizes and with various degrees of substrate surface coverage. These final samples were used for CA measurements. The TEFLON samples were cut from a TEFLON plate grinded with P1000, P1200, P2400 and finally P4000 SiC paper (Struers) This polished TEFLON plate was further treated analogously as the Si-wafer pieces.

B) TEM and SEM images of NP assemblies

Below typical images from the transmission electron microscopy (TEM) measurements are shown to illustrate how the surfaces appear after deposition, and to determine the surface coverage with NPs. Even at the lowest coverage of the surface, there is a tendency that NPs stick on top of each other and cluster together where they land. Example TEM images have been paired with a photo of a drop on a Cu sample surface exposed to the corresponding NP deposition (as shown in the TEM image) during the contact angle measurements.

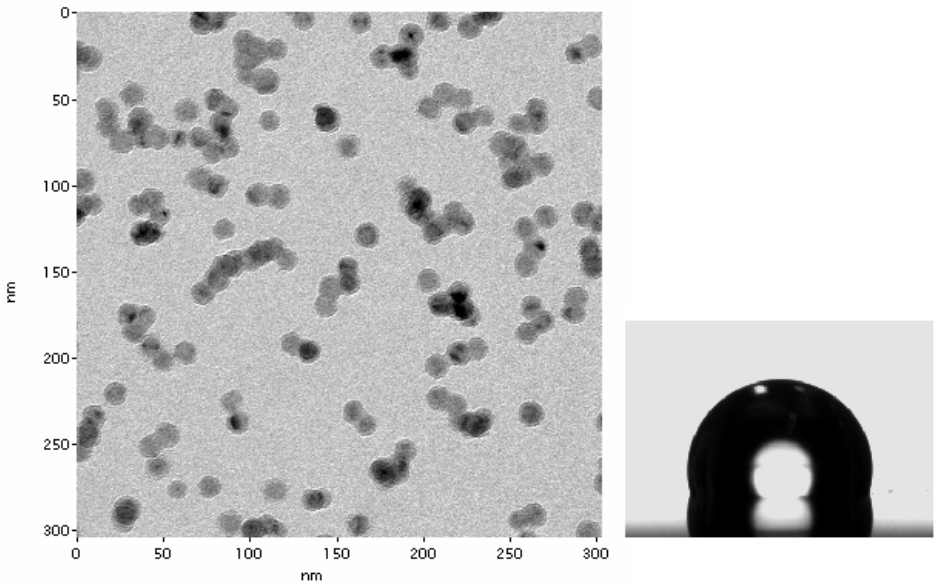

Figure B1: NP average size 14.2 ± 2.1 nm, surface coverage 19.2%, and contact angle 105°.

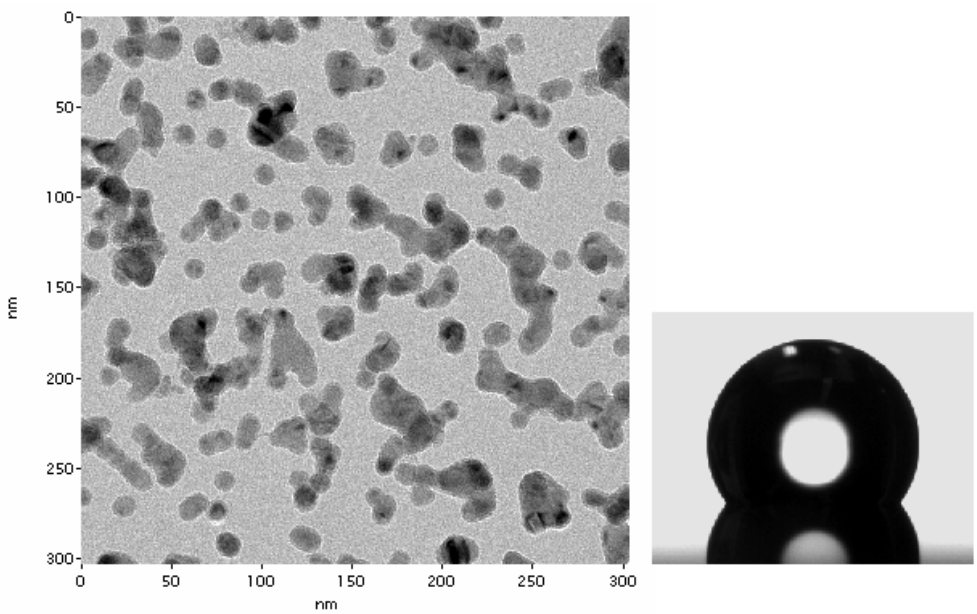

Figure B2: Particle size 12.5 ± 1.8 nm, surface coverage 37.6%, and contact angle 126°.

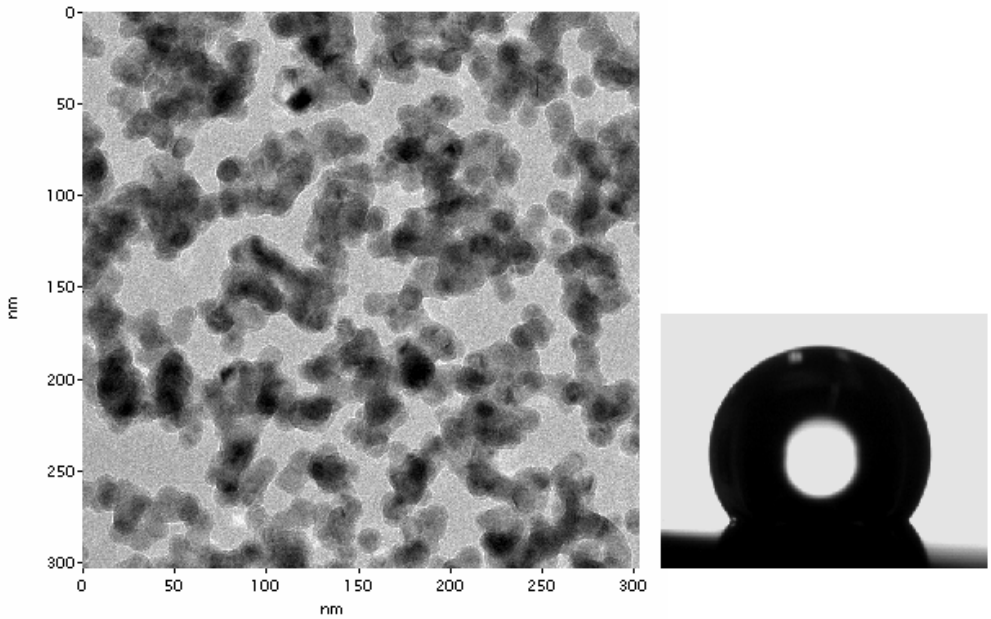

Figure B3: Particle size 13.5 ± 2.5 nm, surface coverage 65.5%, and contact angle 128°.

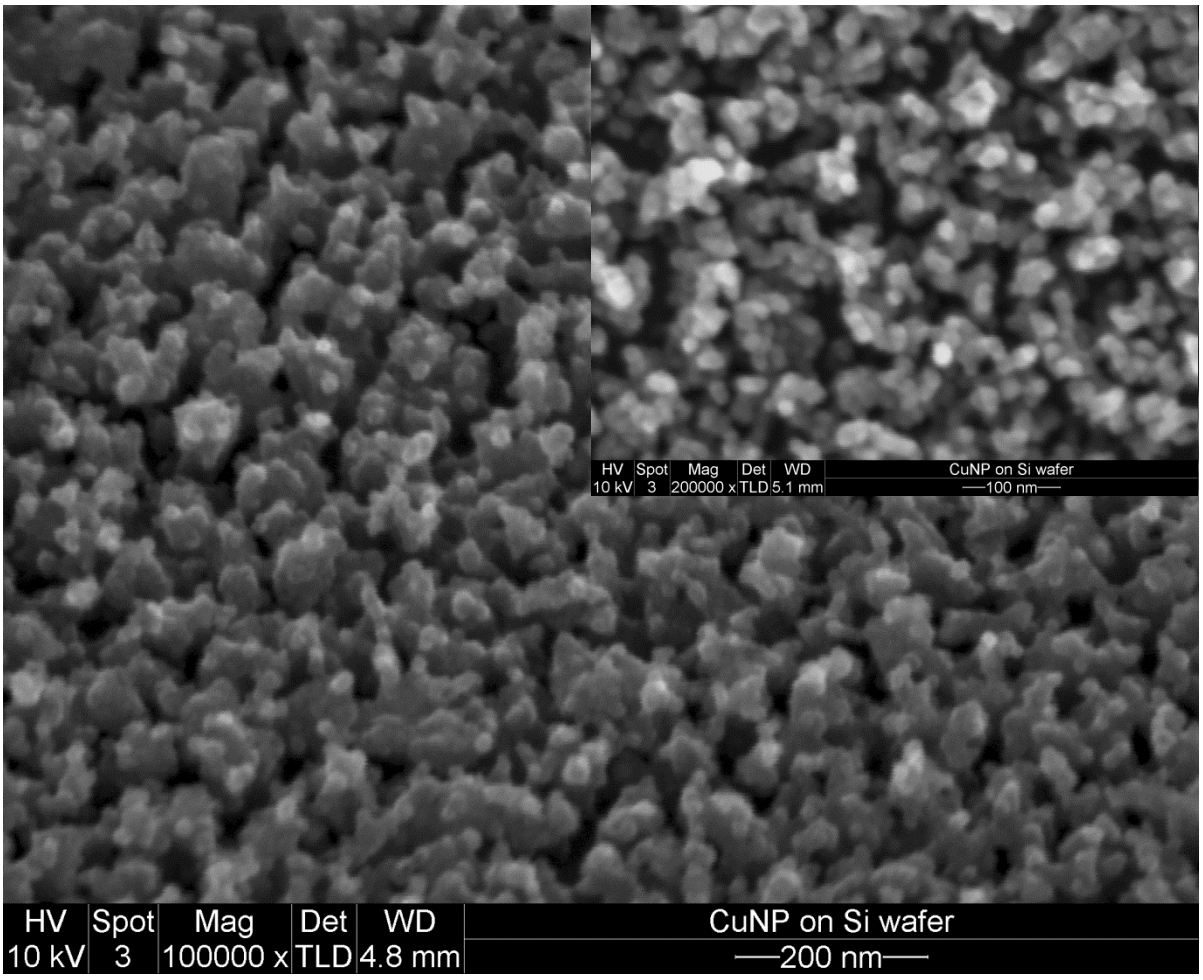

Figure B4: SEM image of NPs within the wetted area around the droplet (Fig. 7c) with the inset showing a similar image of NPs not exposed to water. The latter shows a higher degree of granular structure with more NPs visible.

C) Measurements on pre-roughened surfaces

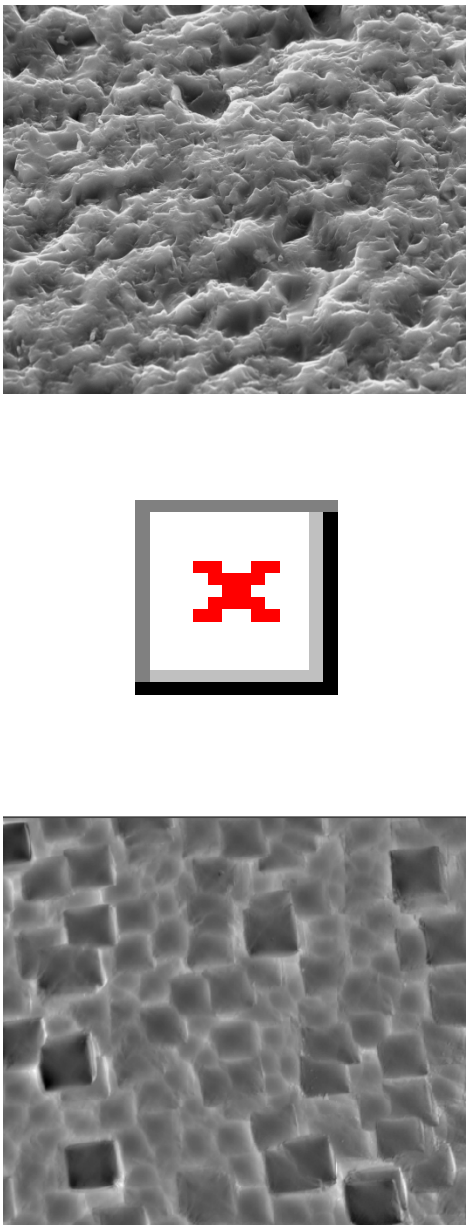

Figure C1 Indicative distinct Si oxide roughened samples prior to NP deposition (Top: Scanning Electron Microscope (SEM) image Solar cell*, Middle: SEM image of Roof tile surface, Bottom: Confocal Microscope image of Si(100) etched surface of 630x630 μm^2 in size). Detailed results of the contact angle measurements can be found in Table C1. The samples were kindly supplied by Hans Hauger from Advanced Wet Technologies GmbH.

Sample	RMS (μm)	NP size (nm)	NP coverage (%)	CA (º)
Flat SiO2	0	0	0	49±4
Nano100 (Etching 15min)	0.21	0	0	44±4
Nano100 (Etching 30min)	0.16	0	0	47±3
Rooftile (Etching 15min)	0.23	0	0	42±2
Rooftile (Etching 30min)	0.41	0	0	47±4
Solar cell template	0.79	0	0	41±3
Nano100 (Etching 15min)	0.21	13(±4)	37%	99±3
Nano100 (Etching 30min)	0.16	13(±4)	23%	99±1
NanoRooftile (Etching 15min)	0.23	13(±4)	37%	108±4
NanoRooftile (Etching 30min)	0.41	13(±4)	23%	98±4
NP solar cell template1	0.79	15(±5)	7%	49±7
NP solar cell template2	0.79	14(±4)	14%	81±2
NP solar cell template3	0.79	15(±6)	40%	85±3

Table C1: Results from the measured Si-oxide surfaces before and after NP deposition. The minutes refer to the etching time of the sample, and 100 refers to Si(100). All the samples were left at least one day after fabrication to allow for the oxide layer to reform completely and minimize surface chemical in homogeneities.